

## MECHANICAL MIXING OF MOLECULAR CRYSTALS

### A green route to co-crystals and coordination networks

D. Braga<sup>\*</sup>, S. L. Giaffreda, M. Curzi, Lucia Maini, M. Polito and Fabrizia Grepioni

Dipartimento di Chimica G. Ciamician, University of Bologna, Via Selmi 2, 40126 Bologna, Italy

Supramolecular reactions between crystalline materials can be exploited to prepare both hydrogen bonded co-crystals and coordination networks. Mechanical mixing of molecular crystals as well as kneading provide an alternative, solvent-free, route to novel materials hence these methods represent a green route to supramolecular solid-state chemistry.

**Keywords:** co-crystals, coordination chemistry, supramolecular solid-state chemistry

### Introduction

The focus of this article is on the idea that reactions between crystalline solids represent a viable alternative method to the preparation of new crystalline materials, i.e. a way to make crystals from crystals. Making crystals by design is the paradigm of crystal engineering [1–8].

Even though our approach encompasses both the possibility of reacting a given crystalline material with another substance (which can be another crystalline material, or a gas) as well as that of transforming a given crystalline material in a different one via a loss/uptake of molecules or a phase transition, we shall describe mainly reactions between solids to obtain new crystalline materials.

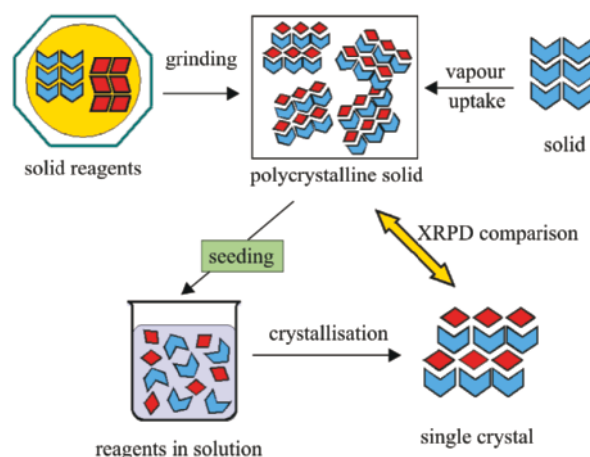
Importantly though, these ‘non-solution’ approaches can be used not only to prepare new materials but also to generate new polymorphic or solvate modifications of the same substance [9–15].

Solid-state reactions activated by grinding or milling are known as mechanochemical reactions. Thus far, mechanochemical processes, and more generally solid-state reactions, have been little exploited at the level of academic research, while they are commonly used at industrial level mainly with inorganic solids and materials [16–18].

Crystalline materials are obtained principally by reactions in the solvent medium and only recently there has been an upsurge of interest in producing crystals by reacting and transforming preformed crystals. In our approach reactions between molecular crystals are regarded as supramolecular reactions, whereby interactions, including coordination bonds, between reactants are broken while those of the product are being formed [9–14].

Solvent-free methods, however, still require that molecules are brought in contact for reaction. In general, fast and quantitative reactions can be achieved when finely ground powders (the large surface area helps molecular diffusion) are exposed to gaseous substances or co-ground with another powder. The two solvent-free processes are distinct but conceptually related, as depicted in the top part of Fig. 1.

In order to define the scopes of this article it is useful to remind the reader that we will not discuss intra-solid reactions, such as topochemical reactions of the type explored by Schmidt [19], which are experiencing a wave of renewed interest [20–27]. We shall also not discuss reactions involving single crystals [28–31]. Amorphous materials though interesting [32, 33], are also outside the scope of this contribution.



**Fig. 1** Schematic representation of the solid–solid and solid–vapour processes and the strategy to obtain single crystals by recrystallisation via seeding. From [15] reproduced by permission of the Royal Society of Chemistry

\* Author for correspondence: dario.braga@unibo.it

Pioneering studies of reactions between molecular crystals were carried out by Rastogi *et al.* about forty years ago [34–36], and extended by Curtin and Paul in the '70's [37–39] and by Etter in the '80's [40–42]. In the case of 2-aminobenzoic acid, Etter also showed that grinding could determine polymorph interconversion [41]. Boldyrev contributions on mechanochemistry have a long tradition in inorganic chemistry [17, 18, 42, 43], and his experience gave important insight also in the organic field [44–46].

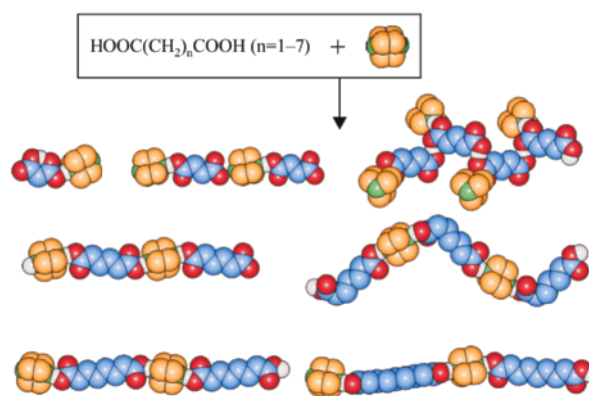
In spite of these early suggestive results, methods based on grinding or ball milling [16, 17, 47] are not very popular in university research labs, while they are commonly used at industrial level [18, 48–50]. Another industrially relevant process that can be applied on a small scale research lab is the so called kneading [51, 52], i.e. the use of a small amount of solvent or of a liquid reactant to speed up a solid-state reactions during grinding or milling [9, 53–55]. Kneading has been described as a sort of 'solvent catalysis' of the solid-state process, whereby the small amount of solvent provides a lubricant for molecular diffusion [9]. The method is commonly employed, for example, in the preparation of cyclodextrin inclusion compounds [51, 52, 56–59]. Jones *et al.* have shown kneading (in their papers called 'solvent drop') can provide a successful means to control the polymorphic outcome of a co-crystallization [55, 60]. The nature of the drop solvent has a crucial role in final form obtained and can induce phase transformation [54] or new polymorphs [61].

In the following we will summarize the results obtained in the mechanochemical preparation of hydrogen bonded adducts and cages as well as of coordination networks.

### Mechanochemical preparation of hydrogen bonded co-crystals

There is a vast literature on the crystal engineering of hydrogen bonded molecular crystals and co-crystals [62–69]. In the organic chemistry area, the mechanochemical formation of hydrogen-bonded co-crystals has been established for some time [70–72].

We have shown that mechanical mixing of solid dicarboxylic acids  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  ( $n=1-7$ ) of variable chain length together with the solid base 1,4-diazabicyclo[2.2.2]octane,  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$ , generates the corresponding salts or cocrystals of formula  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\text{H}[\text{OOC}(\text{CH}_2)_n\text{COOH}]$  ( $n=1-7$ ) (Fig. 2) [73]. The reactions imply transformation of inter-acid  $\text{O}-\text{H}\cdots\text{O}$  bonds into hydrogen bonds of the  $\text{O}-\text{H}\cdots\text{N}$  type between acid and base. The nature (whether neutral  $\text{O}-\text{H}\cdots\text{N}$  or charged  $^-\text{O}\cdots\text{H}-\text{N}^+$ ) of

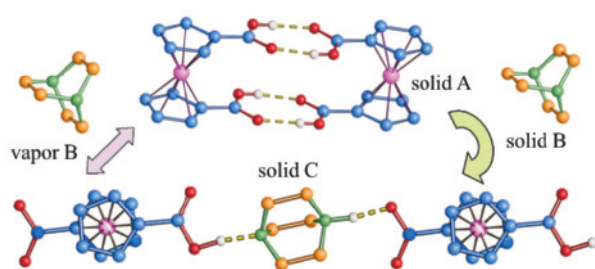


**Fig. 2** The reaction of solid dicarboxylic acids  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  ( $n=1-7$ ) with the solid base 1,4-diazabicyclo[2.2.2]octane,  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$ , generates the corresponding salts or cocrystals of formula  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\text{H}[\text{OOC}(\text{CH}_2)_n\text{COOH}]$  ( $n=1-7$ ). The  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds present in the solid acid are replaced by neutral  $\text{O}-\text{H}\cdots\text{N}$  and charged  $^-\text{O}\cdots\text{H}-\text{N}^+$  interactions, with formation of dimeric units ( $n=1$ ) or infinite chains ( $n=2-7$ ) ( $\text{H}_{\text{CH}}$  atoms not shown for clarity). From [15] reproduced by permission of the Royal Society of Chemistry

the hydrogen bond was established by means of solid-state NMR measurement.

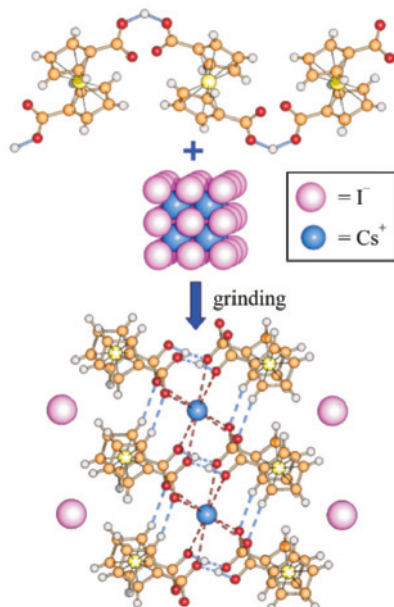
In the organometallic area, the ferrocenyl dicarboxylic acid complex  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{COOH})_2]$  reacts as a polycrystalline solid with solid nitrogen containing bases, such as 1,4-diazabicyclo[2.2.2]octane, 1,4-phenylenediamine, piperazine, *trans*-1,4-cyclohexane-diamine and guanidinium carbonate, generates quantitatively the corresponding organic- organometallic adducts [74, 75]. The example of compound  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{NH}][\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{COOH})(\eta^5-\text{C}_5\text{H}_4\text{COO})]$  is educative (Fig. 3): the same product can be obtained in three different ways: (i) by reaction of solid  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{COOH})_2]$  with vapours of 1,4-diazabicyclo[2.2.2]octane (which possesses a small but significant vapour pressure), (ii) by reaction of solid  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{COOH})_2]$  with solid 1,4-diazabicyclo[2.2.2]octane,  $\text{C}_6\text{H}_{12}\text{N}_2$ , i.e. by co-grinding of the two crystalline powders, and by reaction in MeOH solution of the two reactants. The fastest process is the solid–solid reaction. The base can be removed by mild thermal treatment, and the structure of the starting dicarboxylic acid is regenerated. The processes imply breaking and reassembling of hydrogen-bonded networks, conformational change from *cis* to *trans* of the  $-\text{COO}/-\text{COOH}$  groups on the ferrocene diacid, and proton transfer from acid to base.

Another extremely versatile solid reactant is represented by the organometallic zwitterion  $[\text{Co}^{\text{III}}(\eta^5-\text{C}_5\text{H}_4\text{COOH})(\eta^5-\text{C}_5\text{H}_4\text{COO})]$  [76]. This compound reacts with a number of  $\text{M}^+\text{X}^-$  salts ( $\text{M}^+=\text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$ ;  $\text{X}^-=\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{PF}_6^-$ ) and obtaining compounds of general formula



**Fig. 3** The solid–vapour and solid–solid reactions involving 1,4-diazabicyclo[2.2.2]octane with formation of a linear chain of hydrogen-bonded  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]^-$  anions and monoprotonated  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{NH}]^+$  cations. From [15] reproduced by permission of the Royal Society of Chemistry

$[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]_2\cdot\text{M}^+\text{X}^-$  [77]. In the cases of the  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  salts, the products could only be obtained by kneading. This class of compounds is characterized by the presence of a supramolecular cage formed by four zwitterionic molecules encapsulating the alkali or ammonium cations via  $\text{O}\cdots\text{M}^+$  or  $\text{O}\cdots\text{H}-\text{N}$  interactions. It is fascinating to think of this inter-solid reaction as a sort of sophisticated solid-state ‘solvation’ process of the cations by the organometallic complex [78]. The cage is sustained by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between carboxylic  $-\text{COOH}$  and carboxylate  $-\text{COO}^-$  groups, and by  $\text{C}-\text{H}\cdots\text{O}$  bonds between  $-\text{CH}_\text{C}$  and  $-\text{CO}$  groups, while the anions are layered in between the



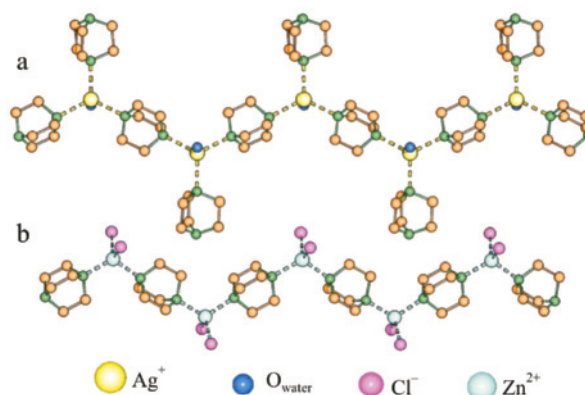
**Fig. 4** A pictorial representation of the process leading from  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$  and  $\text{CsI}$  to  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]_2\cdot\text{Cs}^+\text{I}^-$ . From [15] reproduced by permission of the Royal Society of Chemistry

cationic complexes, as shown in Fig. 4 in the case of  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]_2\cdot\text{Cs}^+\text{I}^-$ .

### Mechanochemical preparation of coordination networks

The preparation of coordination networks is another of the main streams of crystal engineering as witnessed by the literature in this field which is expanding at an exponential pace [29, 79–87].

We have explored the mechanochemical preparation of coordination networks by using bidentate nitrogen bases [88]. The coordination polymer  $\text{Ag}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]_2[\text{CH}_3\text{COO}]\cdot 5\text{H}_2\text{O}$  has been obtained by co-grinding in the solid state and in the air of silver acetate and  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$  in 1:2 ratio (Fig. 5a). The preparation of single crystals of  $\text{Ag}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]_2[\text{CH}_3\text{COO}]\cdot 5\text{H}_2\text{O}$  was obviously indispensable for the determination of the exact nature of the co-grinding product. One could thus establish that the coordination network in  $\text{Ag}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]_2[\text{CH}_3\text{COO}]\cdot 5\text{H}_2\text{O}$  is based on chains of  $\text{Ag}^+\cdots[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\cdots\text{Ag}^+\cdots[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\cdots\text{Ag}^+$ , with each silver atom carrying an extra pendant  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$  ligand and a coordinated water molecule in tetrahedral coordination geometry. When  $\text{ZnCl}_2$  is used instead of  $\text{AgCH}_3\text{COO}$  in the equimolar reaction with  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$ , different products are obtained from solution and solid-state reactions, respectively. Figure 5b shows that the structure of  $\text{Zn}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\text{Cl}_2$ , crystallized from solution, is based on a one-dimensional zig-zag coordination network constituted of alternating  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$  and  $\text{ZnCl}_2$  units, joined by  $\text{Zn}-\text{N}$  bonds. Crystals of the product obtained by grinding have not been obtained and the details of this compound remain unknown. However, we have been able



**Fig. 5** The coordination network in a –  $\text{Ag}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]_2[\text{CH}_3\text{COO}]\cdot 5\text{H}_2\text{O}$  and in b –  $\text{Zn}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\text{Cl}_2$ . From [15] reproduced by permission of the Royal Society of Chemistry



to demonstrate that the phase obtained by co-grinding can be transformed into the known anhydrous phase  $\text{Zn}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]\text{Cl}_2$  by prolonged manual grinding.

Other examples of mechanochemical preparation of coordination complexes are known. Steed and Raston *et al.* have explored the use of mechanochemistry to prepare extended supramolecular arrays [89]. Grinding of  $\text{Ni}(\text{NO}_3)_2$  with 1,10-phenanthroline resulted in the facile preparation of  $[\text{Ni}(1,10\text{-phenanthroline})_3]^{2+}$  accompanied by a dramatic and rapid colour change. Addition of the solid sodium salt of tetrasulfonatocalix[4]arene gives two porous  $\pi$ -stacked supramolecular arrays  $[\text{Ni}(1,10\text{-phenanthroline})_3]_2[\text{tetrasulfonatocalix[4]arene}^{4-}] \cdot n\text{H}_2\text{O}$  and the related  $[\text{Na}(\text{H}_2\text{O})_4(1,10\text{-phenanthroline})][\text{Ni}(1,10\text{-phenanthroline})_3]_4[\text{tetrasulfonatocalix[4]arene}^{4-}][\text{tetrasulfonatocalix[4]arene}^{5-}] \cdot n\text{H}_2\text{O}$  depending on stoichiometry. It has also been reported that the co-grinding of copper(II) acetate hydrate with 1,3-di(4-pyridyl)propane gives a gradual colour change from blue to blue-green in a few minutes. The resulting material was shown by solid state NMR spectroscopy to comprise a 1D coordination polymer with water-filled pores. The same host structure,  $[\{\text{Cu}(\text{OAc})_2\}_2(\mu\text{-}1,3\text{-di}(4\text{-pyridyl})\text{propane})]_n$ , could be obtained from solution containing methanol, acetic acid or ethylene glycol guest species [90].

### Induced polymorphism and solvate formation

As illustrated above, the paradigm of crystal engineering is the possibility of obtaining an ordered and periodical organization of molecules or ions through space from the self-assembly of building blocks. The control of the assembly process depends on our capacity of instructing molecules or molecular ions how to recognize each other and form stable crystal nuclei, that eventually lead to the desired crystalline material. The problem is further complicated by the possibility of obtaining different solvate forms as well as the unexpected crystallization of a new form (serendipitous polymorphism). While serendipitous polymorphism and solvate formation are very common ('it happens' to crystallize the same substance as different crystals or solvates), intentional polymorphism is more difficult, as it requires the purposed investigation of the conditions to obtain different crystals for the same species [91–93].

Thus far we have provided evidence that the solvent-free reaction of a molecular crystal with a vapour can be exploited to make new crystalline supramolecular aggregates. A useful notion is that the same approach can be used to prepare a new polymorph or solvate [94, 95]. This section of the arti-

cle will expand on this idea. We will show how mechanical treatment, vapour uptake and release and seeding can all be used to obtain new crystal forms. We will also discuss the useful possibility of obtaining interconversion of crystal forms as a function of pressure and temperature.

We have come across a case of relationship between polymorphism and pseudo-polymorphism during the initial preparation of the zwitterion  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$  [75]. Single crystals of this molecule could be obtained by seeding a water solution obtained by dissolving the tri-hydrate  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})] \cdot 3\text{H}_2\text{O}$  with seeds prepared by stepwise dehydration of the hydrated species [74].

A thermogravimetric experiment showed that  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})] \cdot 3\text{H}_2\text{O}$  reversibly releases one water molecule at 378 K, while the loss of the two remaining water molecules occurs at ca. 506 K and is immediately followed by a phase transition. Subsequent comparison of the calculated and measured powder diffractograms of the anhydrous phase confirms that the powder obtained at 506 K and the single crystals precipitated at room temperature after seeding possess the same structure. Importantly, crystallization in the absence of seeds of  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$  yields the initial tri-hydrate form  $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})] \cdot 3\text{H}_2\text{O}$ .

In a similar process, crystals of  $[\text{Ru}(\eta_6\text{-C}_6\text{H}_6)_2][\text{BF}_4]_2$  can be crystallized from nitromethane as the solvate form  $[\text{Ru}(\eta_6\text{-C}_6\text{H}_6)_2][\text{BF}_4]_2 \cdot \text{MeNO}_2$ . These solvate crystals, if exposed to air, rapidly convert to the unsolvate form  $[\text{Ru}(\eta_6\text{-C}_6\text{H}_6)_2][\text{BF}_4]_2$ . The nature of this latter compound was established from single crystals obtained from water in the presence of seeds of the powder material obtained from desolvated crystals  $[\text{Ru}(\eta_6\text{-C}_6\text{H}_6)_2][\text{BF}_4]_2 \cdot \text{MeNO}_2$  [96].

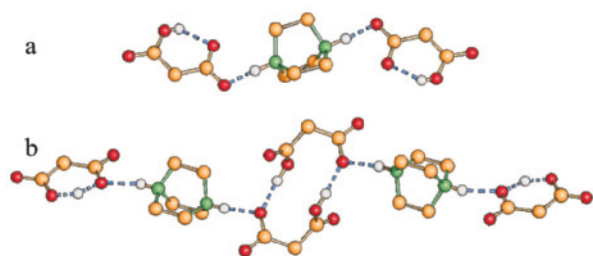
The opposite process, namely solvent uptake, can often be activated by mechanical treatment of unsolvated crystals. There are several reports on that even gentle grinding of a powder product to prepare a sample for powder diffraction may lead to the formation of a hydrated product [41, 97–100]. In our lab, we have seen that the hydrated salt  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]^- \cdot \text{H}_2\text{O}$  is obtained by simply grinding in the air the crystalline powder of  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]^-$  that precipitates from THF or nitromethane on reacting  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$  with  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]$  [101]. Once  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]^- \cdot \text{H}_2\text{O}$  has been obtained by grinding, its single crystals can be grown from water or nitromethane, while crystals of the anhydrous form are no longer observed. However, on heating, the hydrated

form loses water at 373 K and reverts to the starting material.

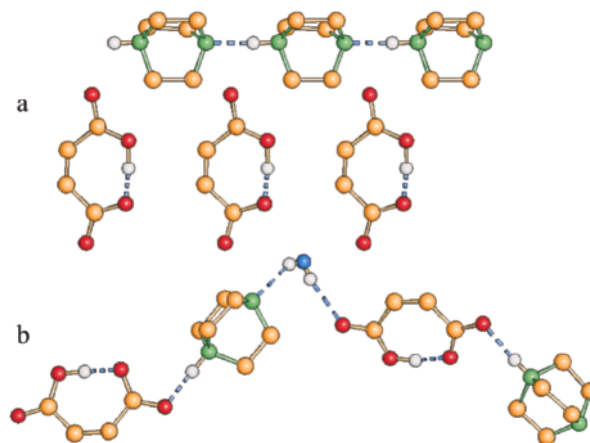
A related situation has been observed on reacting solid  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$  with solid malonic acid  $[\text{HOOC}(\text{CH}_2)\text{COOH}]$  in the molar 1:2 ratio [102]. Two different crystal forms of the salt  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}][\text{OOC}(\text{CH}_2)\text{COOH}]_2$  are obtained depending on preparation technique (grinding or solution) and crystallization speed. Form I, containing mono-hydrogen malonate anions forming conventional intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds and inter-ionic  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, is obtained by solid-state co-grinding or by rapid crystallization, while form II, containing both intermolecular and intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, is obtained by slow crystallization (Fig. 6). Forms I and II do not interconvert, while form I undergoes an order-disorder phase transition on cooling. One can envisage the two crystalline forms as hydrogen bond isomers of the same solid supermolecule.

Proton transfer along a hydrogen bond poses an interesting question about polymorph definition. In fact, proton mobility along a hydrogen bond (say from  $\text{O}-\text{H}\cdots\text{N}$  to  $^-\text{O}\cdots\text{H}-\text{N}^+$ ) may not be associated with a phase transition, even though it implies the formal transformation of a molecular crystal into a molecular salt. This situation has been observed, for instance, for the proton migration along an  $\text{O}-\text{H}\cdots\text{O}$  bond in a co-crystal of urea-phosphoric acid (1:1) as a function of temperature [103]. Mootz and Wiechert, on the other hand, have isolated two co-crystals of pyridine and formic acid: in the 1:1 co-crystal proton transfer from formic acid to pyridine does not take place, while in the 1:4 co-crystal  $\text{N}-\text{H}^+\cdots\text{O}^-$  interactions are present [104]. Examples of this kind are rare, but serve to stress how the phenomenon of polymorphism can be, at times, full of ambiguity.

An intriguing case of interconversion between unsolvate and solvate crystals is observed when  $[\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]$  is reacted with maleic acid



**Fig. 6** a – Form I and b – II of  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}][\text{OOC}(\text{CH}_2)\text{COOH}]_2$  and the hydrogen bonded anion-cation chains present in their crystals. Form I is obtained by solid-state co-grinding or by rapid crystallization, while form II is obtained by slow crystallization. From [15] reproduced by permission of the Royal Society of Chemistry



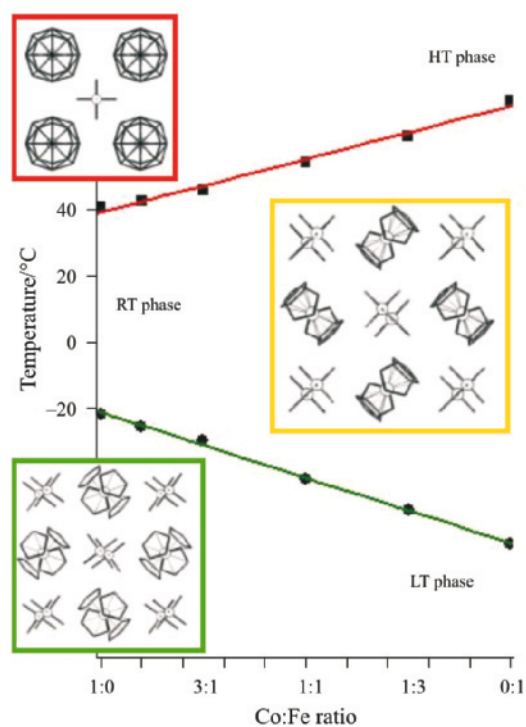
**Fig. 7** Views of the packing and hydrogen bonding in the anhydrous salt a –  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{N}][\text{OOC}(\text{HC}=\text{CH})\text{COOH}]$  and b – of the hydrated salt  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{N}][\text{OOC}(\text{HC}=\text{CH})\text{COOH}]\cdot\text{H}_2\text{O}_{0.25}$ . From [15] reproduced by permission of the Royal Society of Chemistry

$[\text{HOOC}(\text{HC}=\text{CH})\text{COOH}]$ . The initial product is the anhydrous salt  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{N}][\text{OOC}(\text{HC}=\text{CH})\text{COOH}]$ , which contains chains of  $^+\text{N}-\text{H}\cdots\text{N}^-$  bonded cations  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{N}]^+$  and ‘isolated’  $[\text{OOC}(\text{HC}=\text{CH})\text{COOH}]^-$  anions [105]. Upon exposure to humidity the anhydrous salt converts within few hours into the hydrated form  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{N}][\text{OOC}(\text{HC}=\text{CH})\text{COOH}]\cdot 0.25\text{H}_2\text{O}$ , which contains more conventional ‘charge-assisted’  $^+\text{N}-\text{H}\cdots\text{O}^-$  hydrogen bonds between anion and cation (Fig. 7). This latter form can also be obtained by co-grinding.

The two isomorphous crystalline complexes  $[\text{M}(\eta^5-\text{C}_5\text{H}_5)_2][\text{PF}_6]$  ( $M=\text{Co}, \text{Fe}$ ) afford a textbook example of an enantiotropic system, i.e. of polymorphs that interconvert as a function of temperature [106–108]. The room temperature phases of these crystals have been shown, by variable temperature X-ray diffraction experiments and differential scanning calorimetry (DSC), to undergo two reversible solid-to-solid phase changes towards a low temperature monoclinic phase and a high temperature cubic phase, respectively. The only difference between Co and Fe is in the temperatures of the transitions:  $M=\text{Fe}$ , ca. 213.1 and 347.1 K,  $M=\text{Co}$ , ca. 251.8 and 313.9 K measured in the heating cycles, respectively. The phase transitions were investigated by single crystal X-ray diffractometer by collecting data sets on the same crystal specimen. While the room and low temperature phases are ordered, the high temperature phase of  $[\text{Co}(\eta^5-\text{C}_5\text{H}_5)_2][\text{PF}_6]$  contains ordered  $[\text{PF}_6]^-$  anions and orientationally disordered  $[\text{Co}(\eta^5-\text{C}_5\text{H}_5)_2]^+$  cations (Fig. 8), while, in the case of  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2][\text{PF}_6]$ , both cations and anions are disordered.

The close structural similarity between the two complexes  $[M(\eta^5\text{-C}_5\text{H}_5)_2]^+$  ( $M=\text{Co}, \text{Fe}$ ) suggested the possibility of growing crystals from solutions containing mixtures of the two cations. We have discovered that, in the solid state, the two cations are fully miscible in the whole range of composition and that the composition is the same as that of the water solutions from which the mixed-crystals are precipitated, e.g. the mixed salts can be formulated as  $[\text{Co}_x\text{Fe}_{1-x}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  (with  $0 < x < 1$ ). Moreover, the phase transition behaviour depends linearly on the composition (Fig. 8). The temperatures at which the two solid-to-solid phase transitions occur very regularly, as a direct function of the molar ratio, between the two extremes defined by the homo-cationic crystals.

The close structural similarity between the two complexes  $[M(\eta^5\text{-C}_5\text{H}_5)_2]^+$  ( $M=\text{Co}, \text{Fe}$ ) prompted us to explore the possibility of growing crystals from solutions containing mixtures of the two cations. The resulting mixed salts  $[\text{Co}_x\text{Fe}_{1-x}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  (with  $0 < x < 1$ ) show that the two cations are fully miscible in the whole range of composition and that the composition is the same as that of the water solutions from which the mixed-crystals are precipitated. Moreover,

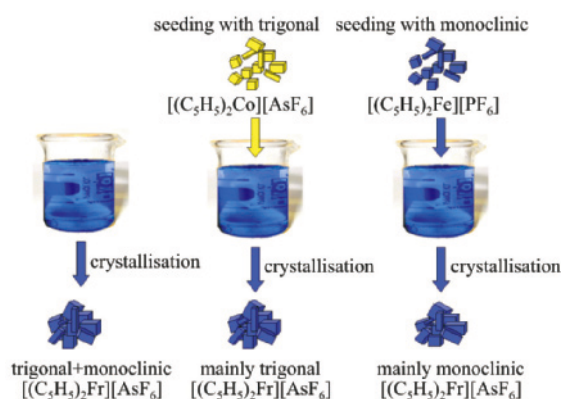


**Fig. 8** Schematic representation of the relationship between the three structures of crystalline  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  ( $M=\text{Co}, \text{Fe}$ ) and the dependence of the phase transition temperatures on the alloy composition, when  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  and  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  are co-crystallized to give  $[\text{Co}_x\text{Fe}_{1-x}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  (with  $0 < x < 1$ ). From [15] reproduced by permission of the Royal Society of Chemistry

the phase transition behaviour depends linearly on the composition, i.e. the temperatures at which the two solid-to-solid phase transitions can be selected by choosing the molar ratio in solution. Thus, the mixed-crystal  $[\text{Co}_x\text{Fe}_{1-x}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ , though composed of molecular ions and soluble in water, possesses the features of an alloy of the  $\text{A}_x\text{B}_{1-x}$  type.

The seeding procedure can also be exploited to attempt crystallization of unyielding materials if seeds of isostructural or quasi-isostructural species that crystallise well are available [109, 110]. This sort of heteromolecular seeding has been instrumental to the separation of two concomitant polymorphs [111]. Precipitation of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  as its  $[\text{AsF}_6]^-$  salt generates two concomitant crystal phases: a trigonal phase (Fe-T) and a monoclinic phase (Fe-M). In order to separate the two polymorphs two solutions were seeded with crystals of the trigonal phase of  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2][\text{AsF}_6]$  and of the monoclinic phase of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ , yielding the corresponding trigonal and monoclinic forms of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{AsF}_6]$ , respectively. The seeding was successful and yielded good quality single crystals of Fe-T and Fe-M (Fig. 9), which proved to be sufficiently robust to undergo a full cycle of four-phase transitions directly on the diffractometer,  $(\text{Fe-T} \rightarrow \text{Fe-M} \rightarrow \text{Fe-C (cubic phase)} \rightarrow \text{Fe-M} \rightarrow \text{Fe-T})$ , a rather uncommon situation that permitted a whole rationalization of the phase transitional behaviour.

On closing the section devoted to polymorphism, we ought to point out that the ongoing intensive research on coordination network crystal engineering is opening new avenues to the investigation of polymorphs and solvates. As a matter of fact the same divergent ligand may yield topologically differ-



**Fig. 9** The seeding procedure where crystals of trigonal  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2][\text{AsF}_6]$  were used to grow the trigonal form of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{AsF}_6]$ , while crystals of monoclinic  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  were used to obtain the monoclinic form of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{AsF}_6]$ . From [15] reproduced by permission of the Royal Society of Chemistry



ent coordination networks with the same metal, which will have the same composition but different architecture (polymorphs or supramolecular isomers?). Moreover, the same network can co-crystallize with a different number and type of molecules in the voids and channels, and these molecules can be desorbed or substituted often without network destruction or reconstruction [112–114]. Solvent and/or guest dependent topological isomerism in coordination polymers has been recently reviewed [115].

## Conclusions

Solid–solid and solid–vapour reactions have been the subject of investigation for decades in the fields of organic and of inorganic chemistry and are commonly used in industrial processes. In spite of this, or – perhaps – because of this, these processes are not very popular in the field of organometallic and coordination chemistry. Clearly, the control on solid-state reactions, that can be used to trap environmentally dangerous or poisonous molecules, is an attractive goal for solid-state chemistry and crystal engineering. For instance, one may purposefully plan to assemble molecules that are capable of absorbing molecules from the gas phase and, possibly, to react with them. This implies sensing and could be exploited to detect molecules if there is a measurable response from the solid state. If the reaction is quantitative and reversible, the same processes (whether based on weak non-covalent bonding or on some type of covalent/ionic, high enthalpy, process) can be used to trap gases and deliver them where appropriate.

Since the solid–solid and solid–vapour reactions described in this article involve formation or disruption of non-covalent interactions, they can be looked at as supramolecular reactions between a two periodical supermolecules (crystals) or between a periodical supermolecule and a molecule in the gas phase. The concept can be stretched to encompass also solvation/desolvation processes, because the uptake/loss of solvent molecules requires supramolecular bond breaking and forming, as for the formation of a co-crystal or a supramolecular adduct. Whether a kneaded reaction between two solid phases can be regarded as a bona fide solid-state process is doubtful, as it is often the case with other mechanochemical reactions, because of the difficulty in controlling exact reaction conditions such as grinding time, temperature, pressure exerted by the operator, etc. The heat generated in the course of a mechanochemical process can induce local melting of crystals or melting at the interface between the different crystals, so that the reaction takes place in the liquid phase even though solid products are ultimately recovered. The same

reasoning applies to formation of eutectic phases [13, 14] and to reactions occurring with a minimal amount of solvent (kneading).

Another point to consider is that the polycrystalline nature of mechanochemical products makes impossible the use of straightforward single-crystal diffraction methods, which are indispensable for a precise description of the structure of the crystal (the ultimate product of a crystal engineering experiment). Beside *ab-initio* structure determination from powder diffraction data [116], which is not yet of widespread application, one has to resort to the *a posteriori* preparation of single crystals starting from the powdered product. In some cases, single crystals can be grown from solution by seeding, i.e. by using a small portion of the polycrystalline sample to ‘instruct’ the crystallization process. Once the single-crystal structure is known, an X-ray powder pattern can be calculated and compared with the measured powder patterns of products obtained from subsequent preparations. As for grinding and kneading, seeding procedures are commonly employed in industries to guarantee crystallization/precipitation of the desired crystal form. Seeds of isostructural or quasi-isostructural species that crystallise well can also be employed to induce crystallisation of unyielding materials (heteromolecular seeding) [117]. Of course, unintentional seeding may also alter the crystallization process in an undesired manner [118].

In conclusion, the use of solvent-free methods, such as mechanical mixing and solid–gas reactions, do not only provide ‘chemical access’ to a variety of new chemicals and/or quantitative transformation of reactants in products [119, 120] can be used to prepare new molecular crystals and co-crystals, a useful notion in crystal engineering.

## Acknowledgements

We thank MIUR (PRIN2004 and FIRB2001) and the University of Bologna for financial support.

## References

- 1 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 98 (1998) 1375.
- 2 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 183 (1999) 117.
- 3 D. Braga, G. R. Desiraju, J. S. Miller, A. G. Orpen and S. L. Price, *Cryst. Eng. Comm.*, 4 (2002) 500.
- 4 D. Braga, L. Brammer and N. R. Champness, *Cryst. Eng. Comm.*, 7 (2005) 1.

- 5 J. Chem. Soc., Dalton Trans. (2000) 3705-3998, Proceedings of the Dalton Discussion on Inorganic Crystal Engineering.
- 6 M. D. Hollingsworth, *Science*, 295 (2002) 2410.
- 7 L. Brammer, *Chem. Soc. Rev.*, 33 (2004) 476.
- 8 M. W. Hosseini, *Cryst. Eng. Comm.*, 6 (2004) 318.
- 9 D. Braga and F. Grepioni, *Angew. Chem. Int. Ed.*, 43 (2004) 4002.
- 10 D. Braga, D. D'Addario, S. L. Giuffreda, L. Maini, M. Polito and F. Grepioni, *Top. Curr. Chem.*, 254 (2005) 71.
- 11 A. V. Trask and W. Jones, *Top. Curr. Chem.*, 254 (2005) 41.
- 12 G. Kaupp, *Top. Curr. Chem.*, 254 (2005) 95.
- 13 G. W. V. Cave, C. L. Raston and J. L. Scott, *Chem. Commun.*, (2001) 2159.
- 14 G. Rothenberg, A. P. Downie, C. L. Raston and J. L. Scott, *J. Am. Chem. Soc.*, 123 (2001) 8701.
- 15 D. Braga and F. Grepioni, *Chem. Commun.*, (2005) 3635.
- 16 J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 71 (1999) 581.
- 17 V. V. Boldyrev and K. Tkacova, *J. Mater. Synth. Process.*, 8 (2000) 121.
- 18 C. Suryanarayana, E. Ivanov and V. V. Boldyrev, *Mater. Sci. Eng., A* 304 (2001) 151.
- 19 G. M. J. Schmidt, *Pure Appl. Chem.*, 27 (1971) 647.
- 20 G. S. Papaefstathiou, A. J. Kipp and L. R. MacGillivray, *Chem. Commun.*, (2001) 2462.
- 21 T. Friscic and L. R. MacGillivray, *Chem. Commun.*, (2005) 5748.
- 22 X. C. Gao, T. Friscic and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 43 (2004) 232.
- 23 L. R. MacGillivray, G. S. Papaefstathiou, T. Friscic, D. B. Varshney and T. D. Hamilton, *Top. Curr. Chem.*, 248 (2004) 201.
- 24 T. Friscic and L. R. Macgillivray, *Chem. Commun.*, (2003) 1306.
- 25 J. Xiao, M. Yang, J. W. Lauher and F. W. Fowler, *Angew. Chem. Int. Ed.*, 39 (2000) 2132.
- 26 J. R. Scheffer and W. J. Xia, *Top. Curr. Chem.*, 254 (2005) 233.
- 27 A. Matsumoto, *Top. Curr. Chem.*, 254 (2005) 263.
- 28 S. Yamamoto, K. Matsuda and M. Irie, *Angew. Chem. Int. Ed.*, 42 (2003) 1636.
- 29 M. Morimoto, S. Kobatake and M. Irie, *Chem. Eur. J.*, 9 (2003) 621.
- 30 M. Irie, S. Kobatake and M. Horichi, *Science*, 291 (2001) 1769.
- 31 K. Novak, V. Enkelmann, G. Wegner and K. B. Wagener, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 1614.
- 32 L. Yu, *Adv. Drug Delivery Rev.*, 48 (2001) 27.
- 33 Y. Shirota, *J. Mater. Chem.*, 15 (2005) 75.
- 34 R. P. Rastogi, P. S. Bassi and S. L. Chadha, *J. Phys. Chem.-Us*, 67 (1963) 2569.
- 35 R. P. Rastogi and N. B. Singh, *J. Phys. Chem.-Us*, 72 (1968) 4446.
- 36 T. P. Rastogi and N. B. Singh, *J. Phys. Chem.-Us*, 70 (1966) 3315.
- 37 A. O. Patil, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 106 (1984) 348.
- 38 C. C. Chiang, C. T. Lin, H. J. Wang, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 99 (1977) 6303.
- 39 I. C. Paul and D. Y. Curtin, *Acc. Chem. Res.*, 6 (1973) 217.
- 40 M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.*, 115 (1993) 4411.
- 41 W. H. Ojala and M. C. Etter, *J. Am. Chem. Soc.*, 114 (1992) 10288.
- 42 F. K. Urakaev, V. S. Shevchenko and V. V. Boldyrev, *Dokl. Phys. Chem.*, 377 (2001) 59.
- 43 V. V. Boldyrev, *Ultrason. Sonochem.*, 2 (1995) S143.
- 44 M. A. Mikhailenko, T. N. Drebushchak, V. A. Drebushchak, E. V. Boldyreva and V. V. Boldyrev, *J. Cryst. Growth*, 274 (2005) 569.
- 45 V. V. Boldyrev, *J. Mater. Sci.*, 39 (2004) 5117.
- 46 M. A. Mikhailenko, T. P. Shakhshneider and V. V. Boldyrev, *J. Mater. Sci.*, 39 (2004) 5435.
- 47 G. Kaupp, *Cryst. Eng. Comm.*, 5 (2003) 117.
- 48 J. M. Cairney, S. G. Harris, L. W. Ma, P. R. Munroe and E. D. Doyle, *J. Mater. Sci.*, 39 (2004) 3569.
- 49 Y. A. Kim, T. Hayashi, Y. Fukai, M. Endo, T. Yanagisawa and M. S. Dresselhaus, *Chem. Phys. Lett.*, 355 (2002) 279.
- 50 K. Wiczorek-Ciurawa, K. Gamrat and K. Fela, *Solid State Ionics*, 164 (2003) 193.
- 51 S. Watano, T. Okamoto, M. Tshuri, I. Koizumi and Y. Osako, *Chem. Pharm. Bull.*, 50 (2002) 341.
- 52 S. Watano, J. Furukawa, K. Miyamoto and Y. Osako, *Adv. Powder Technol.*, 12 (2001) 427.
- 53 N. Shan, F. Toda and W. Jones, *Chem. Commun.*, (2002) 2372.
- 54 A. V. Trask, N. Shan, W. D. S. Motherwell, W. Jones, S. Feng, R. B. H. Tan and K. J. Carpenter, *Chem. Commun.*, (2005) 880.
- 55 A. V. Trask, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, (2004) 890.
- 56 N. Morin, A. Chilouet, J. Millet and J. C. Rouland, *J. Therm. Anal. Cal.*, 62 (2000) 187.
- 57 G. Bruni, A. Marini, V. Berbenni, R. Riccardi and M. Villa, *J. Inclusion Phenom. Macr. Chem.*, 35 (1999) 517.
- 58 F. Taneri, T. Gueneri, Z. Aigner and M. Kata, *J. Inclusion Phenom. Macr. Chem.*, 44 (2002) 257.
- 59 R. Saikosin, T. Limpaseni and P. Pongsawasdi, *J. Inclusion Phenom. Macr. Chem.*, 44 (2002) 191.
- 60 A. V. Trask, W. D. S. Motherwell and W. Jones, *Cryst. Growth Des.*, 5 (2005) 1013.
- 61 A. V. Trask, D. A. Haynes, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, (2006) 51.
- 62 M. J. Zaworotko, *Chem. Soc. Rev.*, 23 (1994) 283.
- 63 T. Steiner, *Angew. Chem. Int. Ed.*, 41 (2002) 48.
- 64 M. J. Calhorda, *Chem. Commun.*, (2000) 801.
- 65 D. Braga, L. Maini, M. Polito and F. Grepioni, *Struct. Bonding*, 111 (2004) 1.
- 66 M. Nishio, *Cryst. Eng. Comm.*, 6 (2004) 130.
- 67 L. Brammer, *Dalton Trans.*, (2003) 3145.
- 68 A. D. Burrows, *Struct. Bonding*, 108 (2004) 55.
- 69 A. Nangia, *Cryst. Eng. Comm.*, (2002) 1.
- 70 M. C. Etter and G. M. Frankenbach, *Chem. Mater.*, 1 (1989) 10.
- 71 V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, (1996) 987.
- 72 M. R. Cairra, L. R. Nassimbeni and A. F. Wildervanck, *J. Chem. Soc., Perkin Trans.*, 2 (1995) 2213.



- 73 D. Braga, L. Maini, G. de Sanctis, K. Rubini, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem. Eur. J.*, 9 (2003) 5538.
- 74 D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Eur. J.*, 9 (2003) 4362.
- 75 D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Commun.*, (2002) 2960.
- 76 D. Braga, L. Maini, M. Polito and F. Grepioni, *Organometallics*, 18 (1999) 2577.
- 77 D. Braga, L. Maini, M. Polito and F. Grepioni, *Chem. Commun.*, (2002) 2302.
- 78 D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem. Eur. J.*, 10 (2004) 3261.
- 79 A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schroder, *Coord. Chem. Rev.*, 222 (2001) 155.
- 80 L. Pan, M. B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath and J. K. Johnson, *J. Am. Chem. Soc.*, 126 (2004) 1308.
- 81 F. A. Cotton, C. Lin and C. A. Murillo, *J. Chem. Soc., Dalton Trans.*, (2001) 499.
- 82 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 300 (2003) 1127.
- 83 N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *Cryst. Eng. Comm.*, 4 (2002) 401.
- 84 M. Oh, J. A. Reingold, G. B. Carpenter and D. A. Sweigart, *Coord. Chem. Rev.*, 248 (2004) 561.
- 85 S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 246 (2003) 103.
- 86 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 246 (2003) 247.
- 87 K. Biradha and M. Fujita, *Angew. Chem. Int. Ed.*, 41 (2002) 3392.
- 88 D. Braga, S. L. Giaffreda, F. Grepioni and M. Polito, *Cryst. Eng. Comm.*, 6 (2004) 458.
- 89 P. J. Nichols, C. L. Raston and J. W. Steed, *Chem. Commun.*, (2001) 1062.
- 90 W. J. Belcher, C. A. Longstaff, M. R. Neckenig and J. W. Steed, *Chem. Commun.*, (2002) 1602.
- 91 W. C. McCrone, *Physics and Chemistry of the Organic Solid State*, John Wiley and Sons, 1965 p. 726.
- 92 J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press, Oxford 2002, p. 352.
- 93 J. O. Henck, J. Bernstein, A. Ellern and R. Boese, *J. Am. Chem. Soc.*, 123 (2001) 1834.
- 94 D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 29 (2000) 229.
- 95 D. Braga and F. Grepioni, *Top. Organomet. Chem.*, 4 (1999) 47.
- 96 D. Braga, G. Cojazzi, A. Abati, L. Maini, M. Polito, L. Scaccianoce and F. Grepioni, *Dalton*, (2000) 3969.
- 97 M. R. Caira, *Top. Curr. Chem.*, 198 (1998) 163.
- 98 M. R. Caira, L. R. Nassimbeni and M. Timme, *J. Pharm. Sci.*, 84 (1995) 884.
- 99 R. J. Webb, T. Y. Dong, C. G. Pierpont, S. R. Boone, R. K. Chadha and D. N. Hendrickson, *J. Am. Chem. Soc.*, 113 (1991) 4806.
- 100 M. M. De Villiers, J. G. Van der Watt and A. P. Lotter, *Drug Dev. Ind. Pharm.*, 17 (1991) 1295.
- 101 D. Braga, L. Maini and F. Grepioni, *Chem. Commun.*, (1999) 937.
- 102 D. Braga and L. Maini, *Chem. Commun.*, (2004) 976.
- 103 C. C. Wilson, *Acta Crystallogr., Sect. B: Struct. Sci.*, B57 (2001) 435.
- 104 D. Wiechert and D. Mootz, *Angew. Chem. Int. Ed.*, 38 (1999) 1974.
- 105 D. Braga, K. Rubini and L. Maini, *Cryst. Eng. Comm.*, 6 (2004) 236.
- 106 D. Braga, L. Scaccianoce, F. Grepioni and S. M. Draper, *Organometallics*, 15 (1996) 4675.
- 107 F. Grepioni, G. Cojazzi, S. M. Draper, N. Scully and D. Braga, *Organometallics*, 17 (1998) 296.
- 108 D. Braga, D. Paolucci, G. Cojazzi and F. Grepioni, *Chem. Commun.*, (2001) 803.
- 109 R. J. Davey, N. Blagden, G. D. Potts and R. Docherty, *J. Am. Chem. Soc.*, 119 (1997) 1767.
- 110 H. Koshima and M. Miyauchi, *Cryst. Growth Des.*, 1 (2001) 355.
- 111 D. Braga, G. Cojazzi, D. Paolucci and F. Grepioni, *Cryst. Eng. Comm.*, 3 (2001) 159.
- 112 A. J. Blake, N. R. Brooks, N. R. Champness, M. Crew, A. Deveson, D. Fenske, D. H. Gregory, L. R. Hanton, P. Hubberstey and M. Schroder, *Chem. Commun.*, (2001) 1432.
- 113 D. V. Soldatov, J. A. Ripmeester, S. I. Shergina, I. E. Sokolov, A. S. Zanina, S. A. Gromilov and Y. A. Dyadin, *J. Am. Chem. Soc.*, 121 (1999) 4179.
- 114 B. Rather and M. J. Zaworotko, *Chem. Commun.*, (2003) 830.
- 115 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 101 (2001) 1629.
- 116 K. D. M. Harris and E. Y. Cheung, *Chem. Soc. Rev.*, 33 (2004) 526.
- 117 P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B: Struct. Sci.*, B38 (1982) 1741.
- 118 J. D. Dunitz and J. Bernstein, *Acc. Chem. Res.*, 28 (1995) 193.
- 119 G. Kaupp, *Cryst. Eng. Comm.*, (2006) DOI: 10.1039/b609053b.
- 120 F. Toda and Editor, *Organic Solid State Reactions*, Springer, Berlin, Germany 2005, p. 305.

---

DOI: 10.1007/s10973-007-8484-y